Short-pulse x-rays at the APS: Rapid Chemical and Physical Processes in Solution

Argonne National Laboratory
Advanced Photon Source
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A Survey of Some Time-Resolved X-ray Experiments on Condensed-Phase Chemical Systems

Anfinrud & Wulff- Photodissociation in Heme Protein Crystals

Wulff- Photodissociation of I_2, CH_3I and $C_2H_4I_2$

Bressler and Chergui- Excited State Dynamics of Ru(II)$(bpy)_3$

Rose-Petruck- Ligand dissociation of $Fe_2(CN)_{10}$

Chen- Ni(TPP) Excited-state Geometry Changes and Ligation

Schoenlein- Fe(II) Differential EXAFS

Marcus theory for (non-adiabatic) electron-transfer

Motivations: Photo-electrochemistry for solar energy conversion

$$k_{et} = \frac{2\pi}{\hbar} \left| H_{DA} \right|^2 \frac{1}{\sqrt{4\pi k_B T}} \exp\left(\frac{-\left(\lambda + \Delta G^{\circ}\right)^2}{4\lambda k_B T} \right)$$

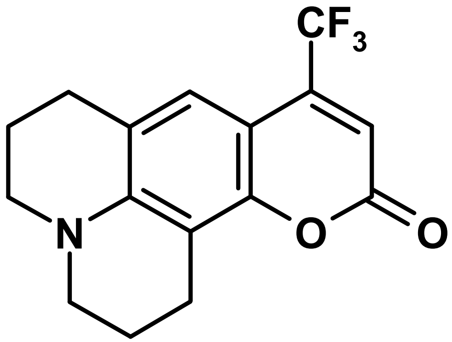
$$\lambda = \lambda_{\mathbf{vibrational}} + \lambda_{\mathbf{solvation}}$$

For large R_{DA} and low k_{et}, $\langle \mathrm{H}_{\mathbf{DA}} \rangle \propto \exp\left(-\beta\, \mathbf{R}_{\mathbf{DA}}\right)$

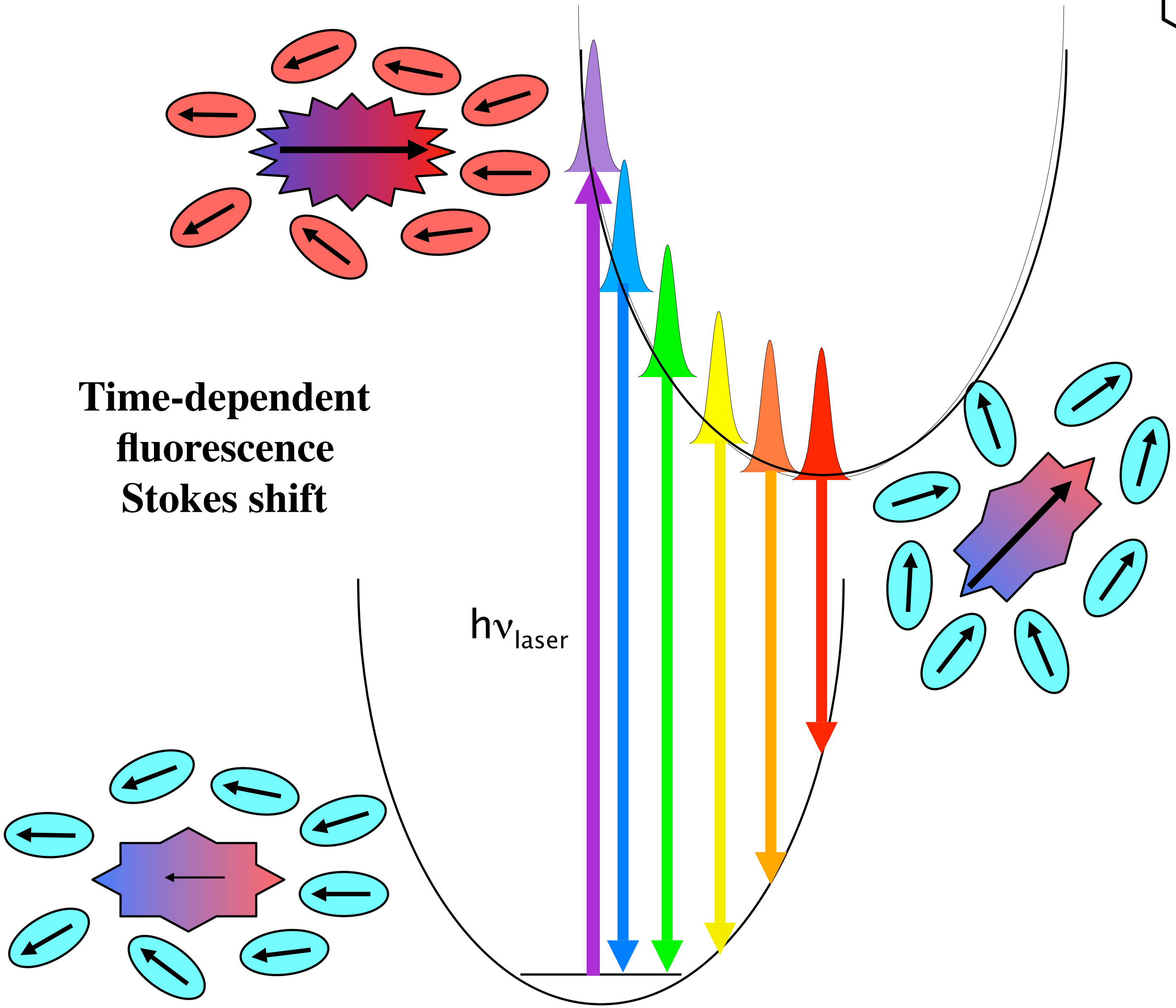
For small R_{DA}, H_{DA} has strong angular dependence.

Marcus, R.A. ***Rev. of Modern Phys.*** **1993,** ***65, 599-610. (Nobel Lecture)***
Marcus, R.A.; Sutin, N. ***Biochim. Biophys. Acta*** **1985,** ***811*****, 2655.**

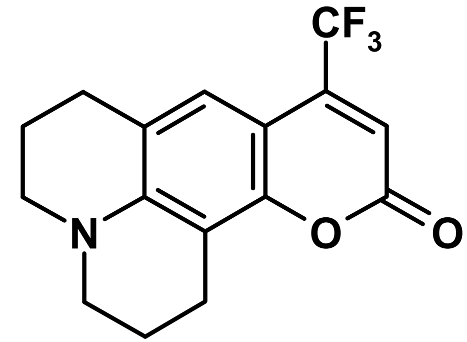
Transient solvation in dipolar liquids



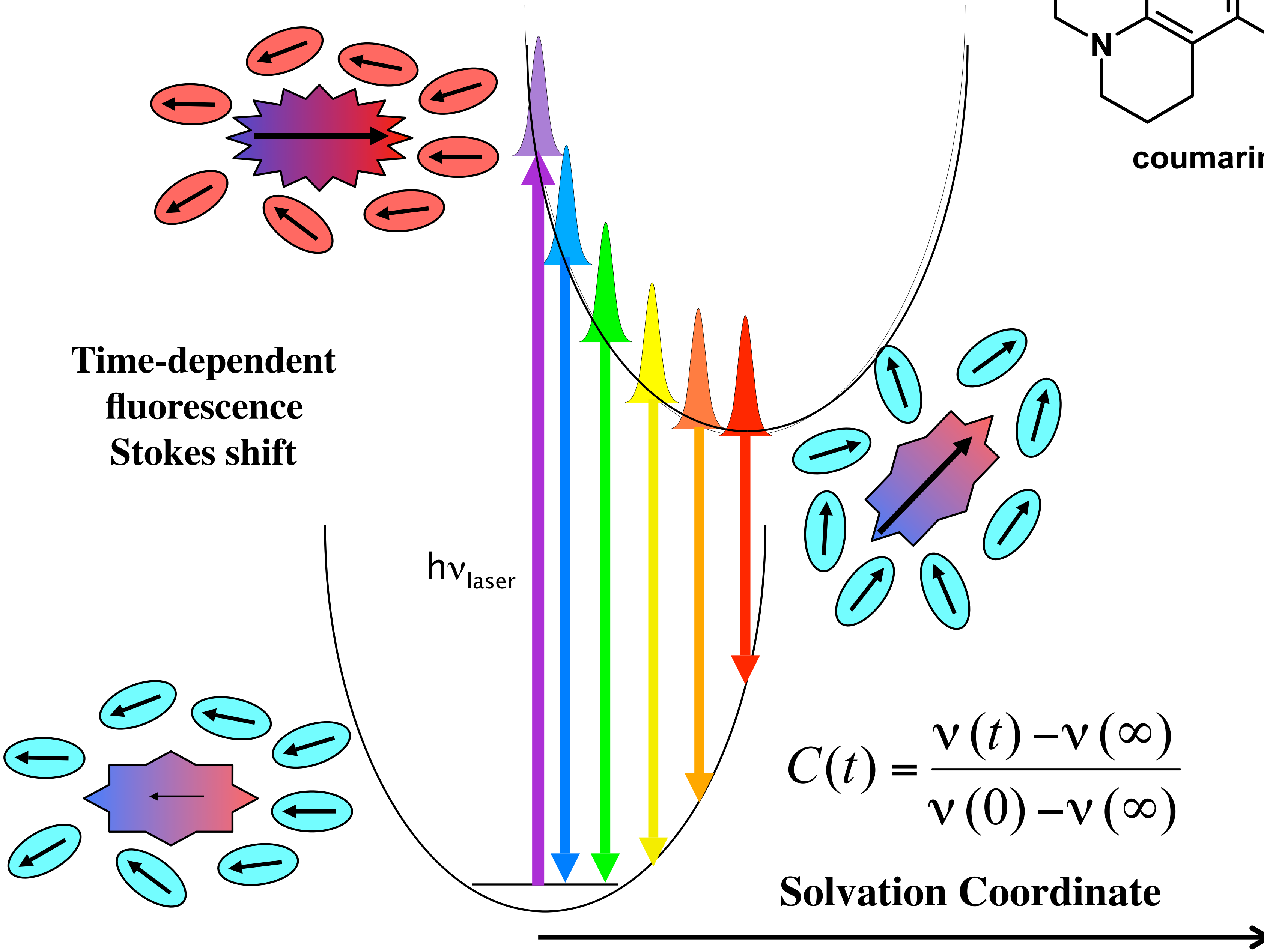
coumarin 153



Transient solvation in dipolar liquids



coumarin 153



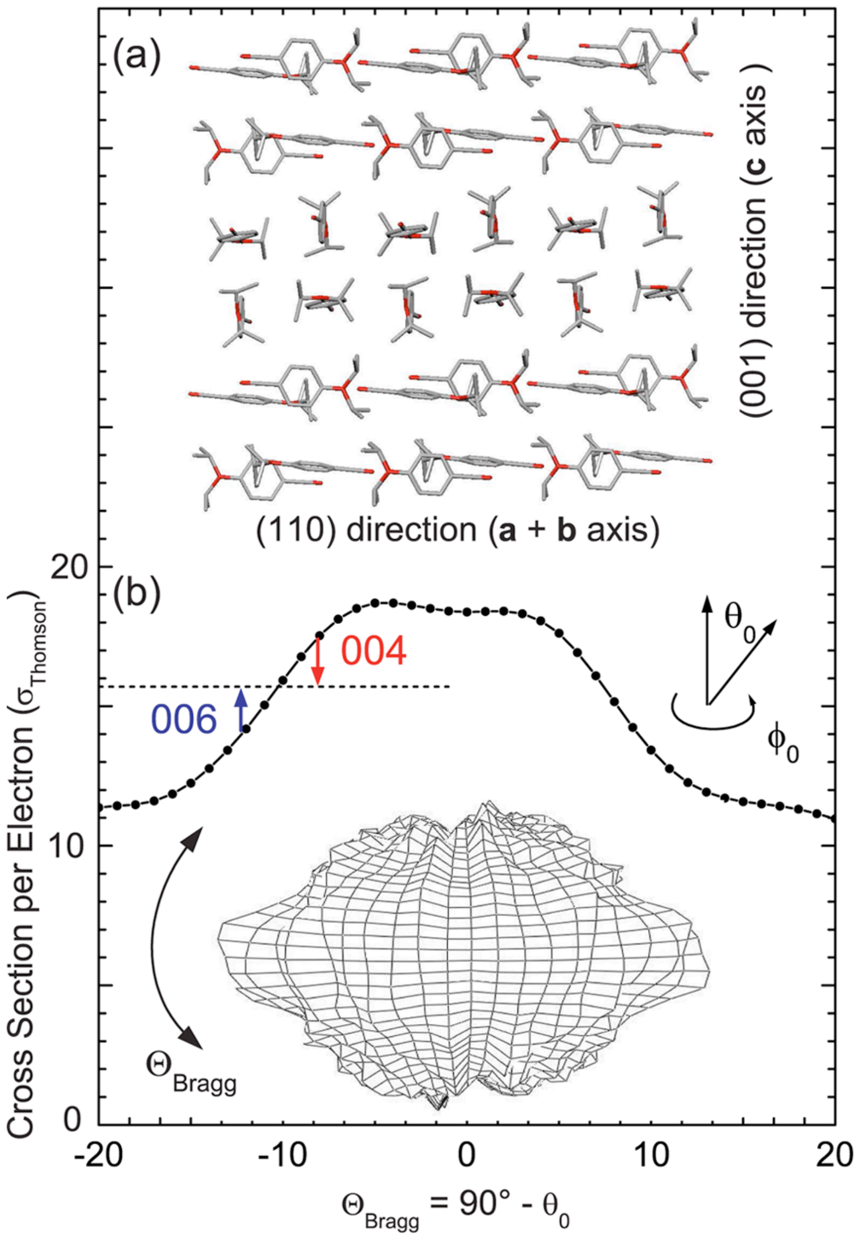
$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

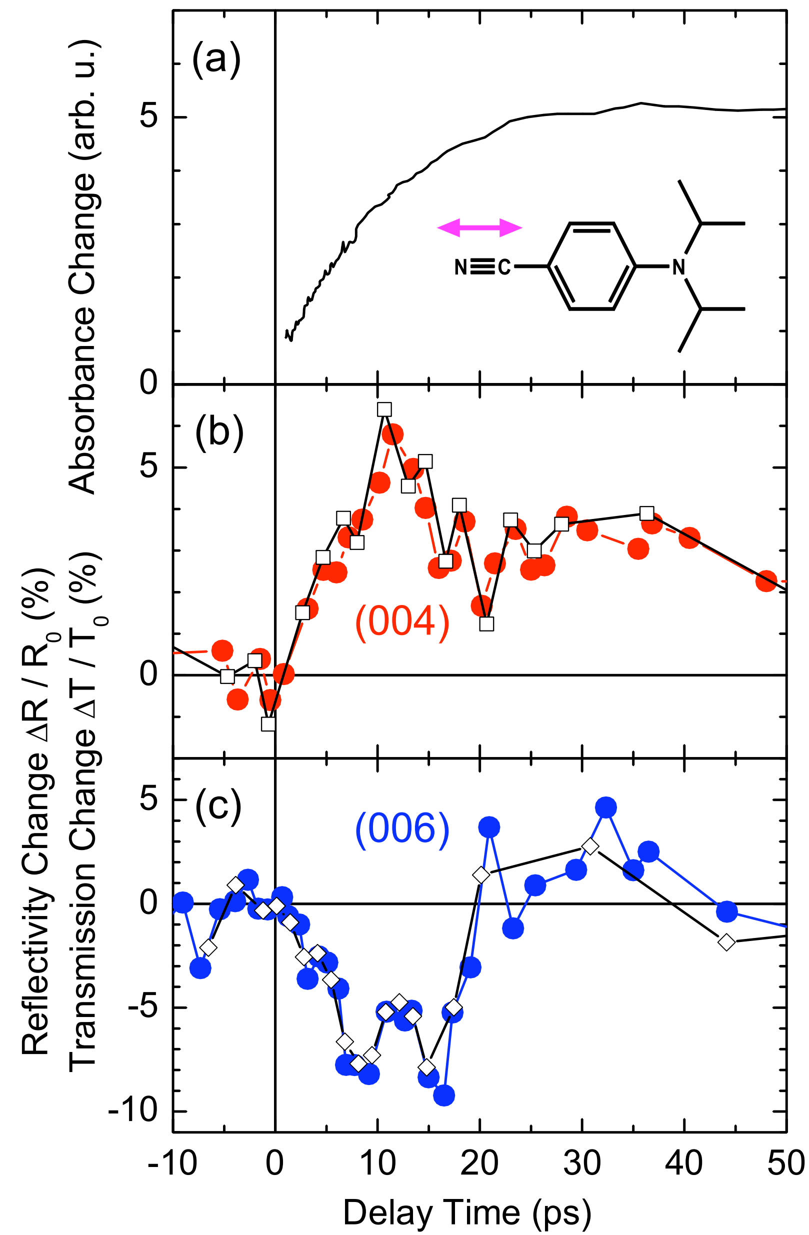
Laser-Induced Time-resolved X-ray Diffraction LITR-XRD (Bragg diffraction):

Structural response to photo-induced dipolar solvation response in a crystal

Ultrafast Changes of Molecular Crystal Structure Induced by Dipole Solvation

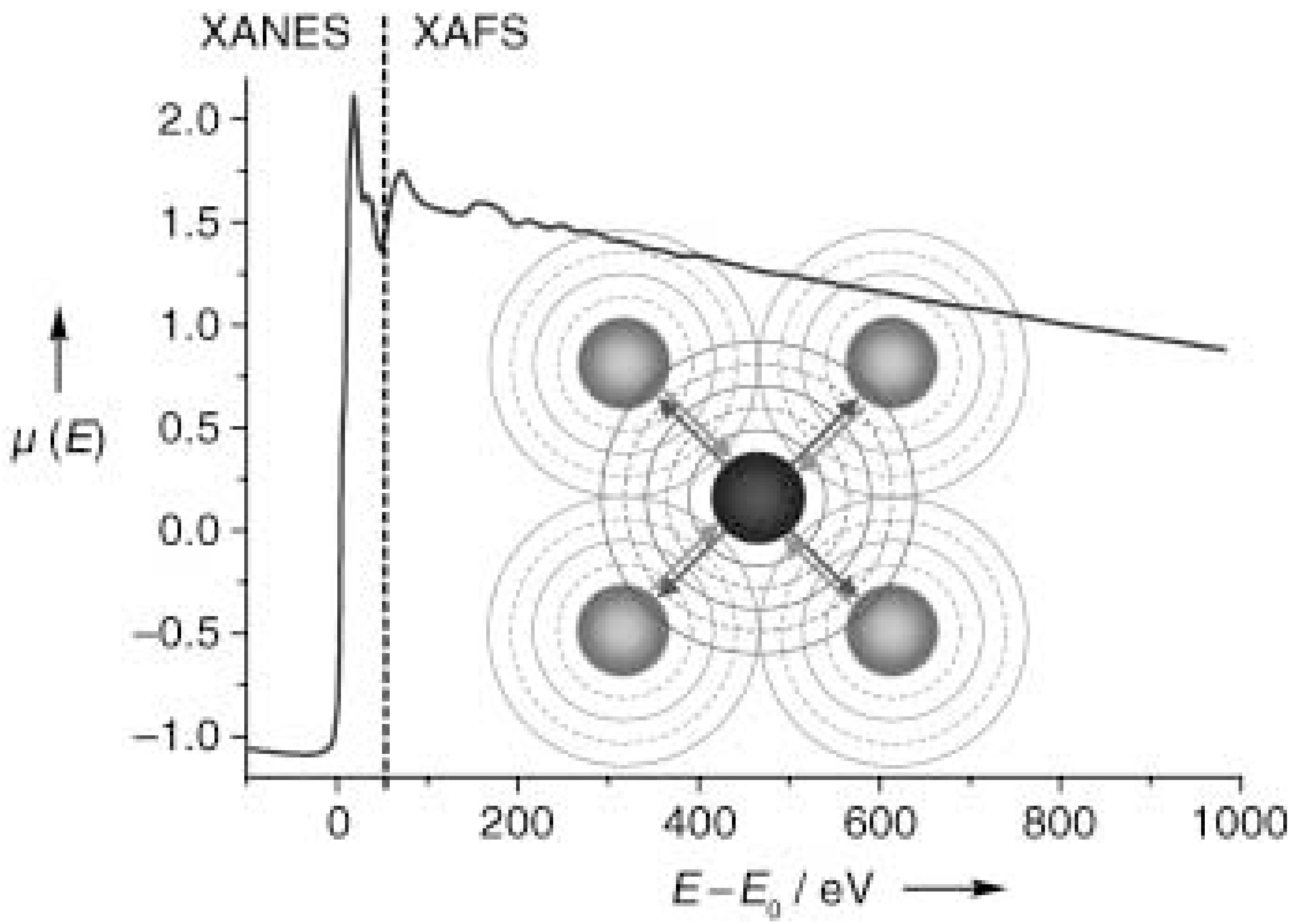
M. Braun,[1] C. v. Korff Schmising,[2] M. Kiel,[2] N. Zhavoronkov,[2] J. Dreyer,[2] M. Bargheer,[2] T. Elsaesser,[2] C. Root,[1]
T. E. Schrader,[1] P. Gilch,[1] W. Zinth,[1] and M. Woerner[2,*]





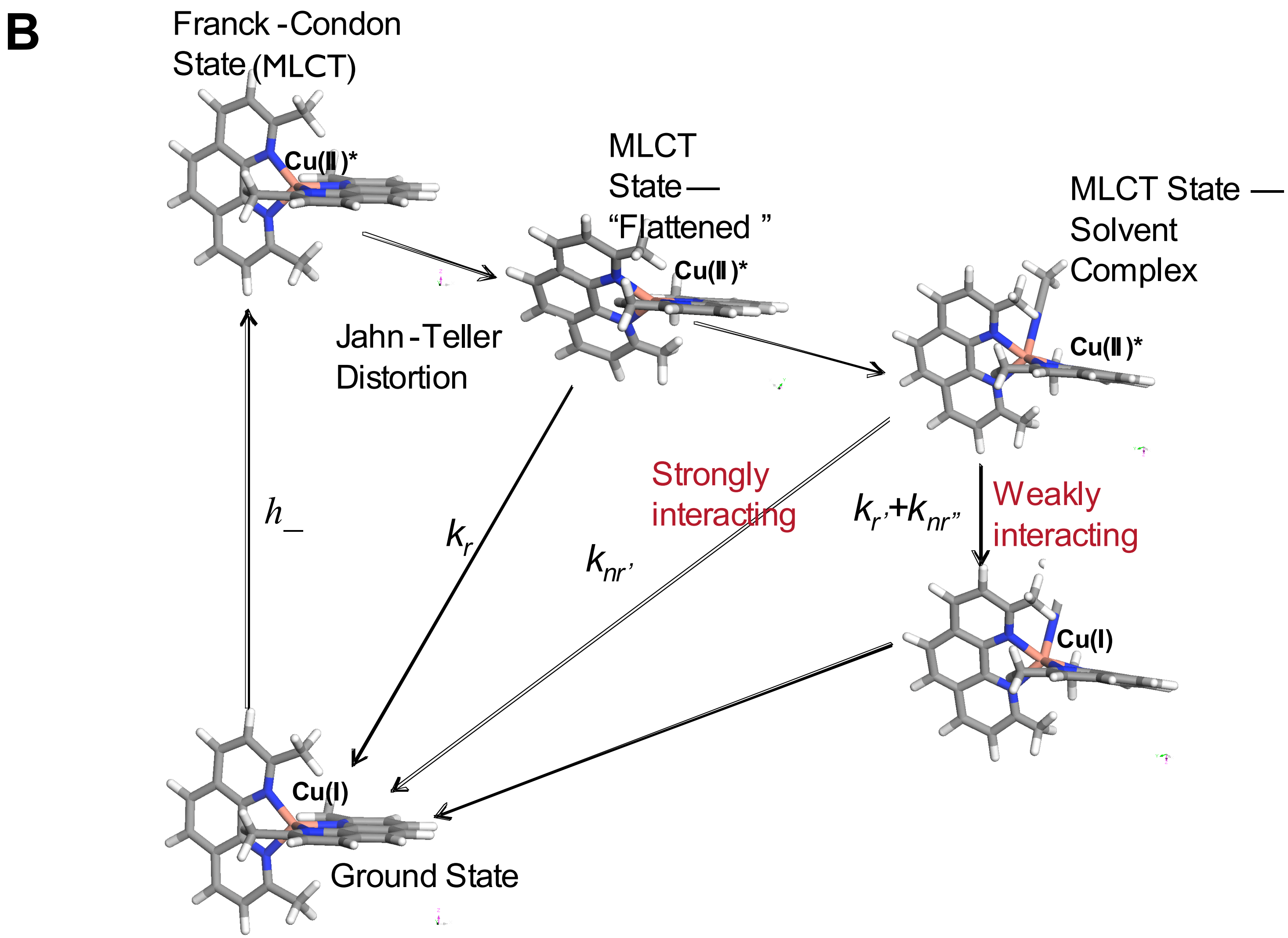
Applications of Laser-Induced Time-Resolved X-ray Absorption Spectroscopy (LITR-XAS)

X-ray Absorption Spectroscopy: XANES and XAFS



L. X. Chen, Angewandte Chemie Int. Ed. 2004, 43, 2886-2905

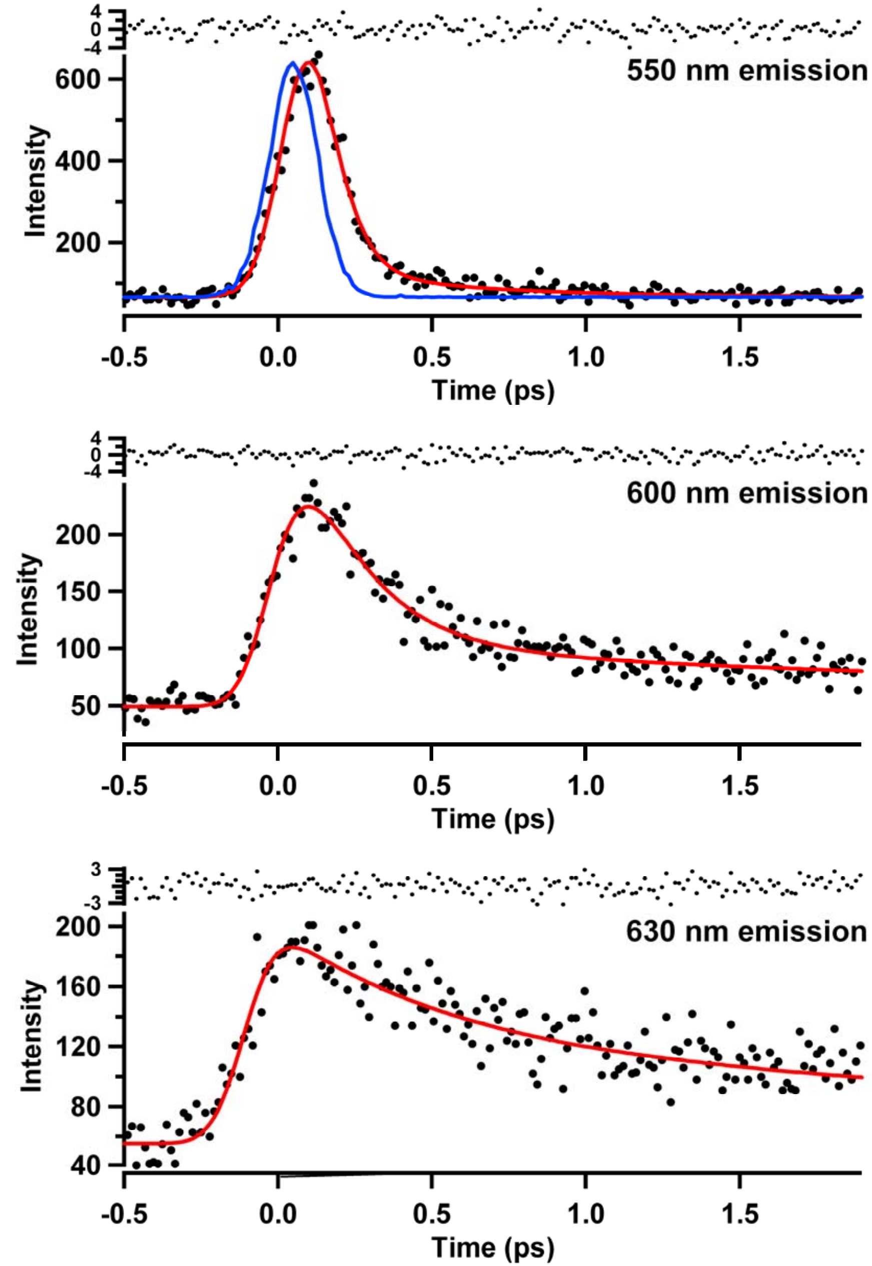
Understanding the Complex Photophysics of $Cu(I)(dmp)_2$



George B. Shaw,[†,‡] Christian D. Grant,[§,||] Hideaki Shirota,[§] Edward W. Castner Jr.,[§,*]
Gerald J. Meyer,[⊥] and Lin X. Chen*[,†]

J. AM. CHEM. SOC. 2007, *129*, 2147−2160 ■ 2147

Time-Resolved Emission of $Cu(I)(dmp)_2$ in CH_3CN Solution



Spin-interconversion from ^{1}MLCT to ^{3}MLCT

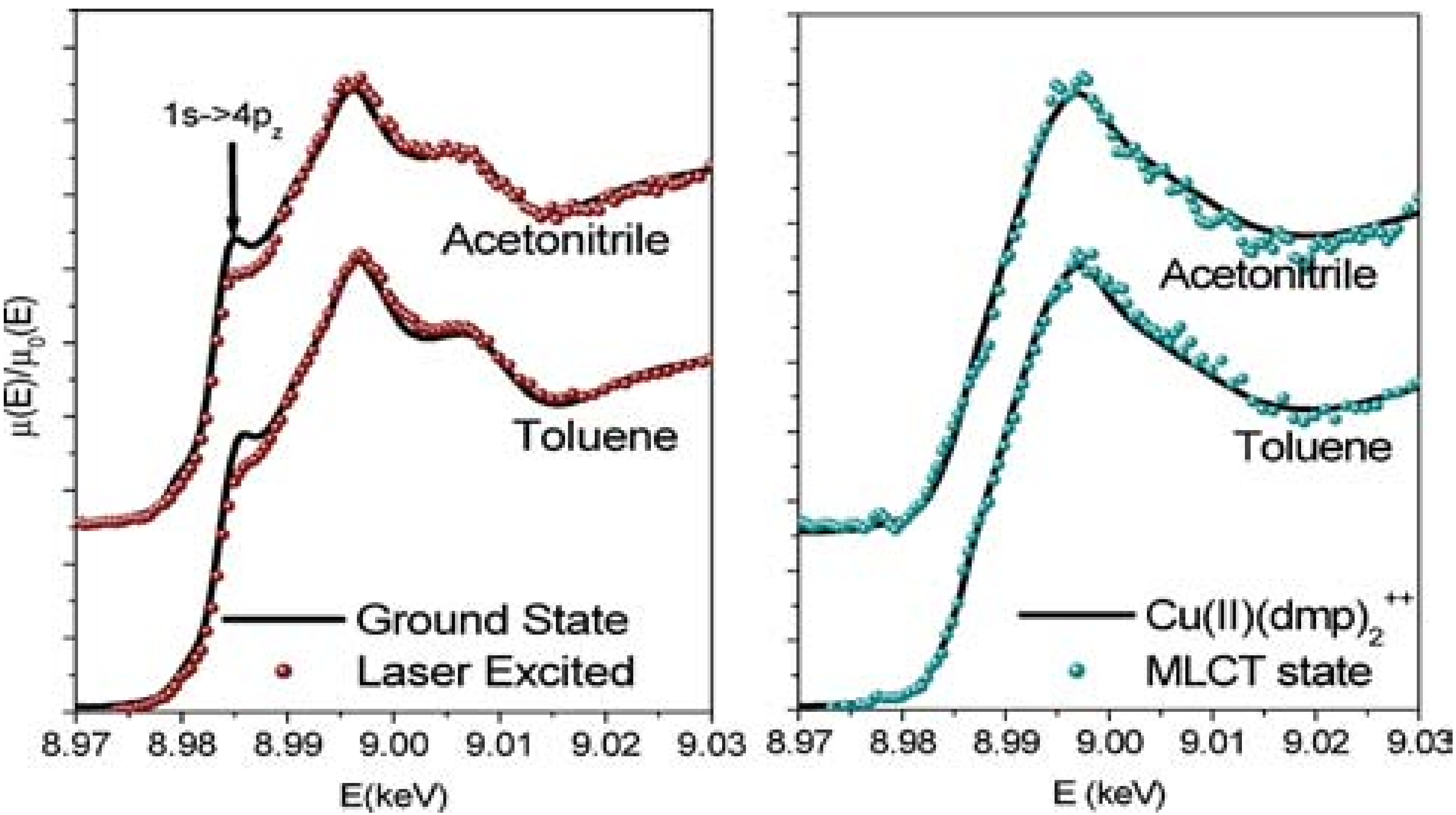
and

geometric relaxation from tetrahedral Cu(I) to square-planar Cu(II)

George B. Shaw,[†,‡] Christian D. Grant,[§,||] Hideaki Shirota,[§] Edward W. Castner Jr.,[§,*]
Gerald J. Meyer,[⊥] and Lin X. Chen[*,†]

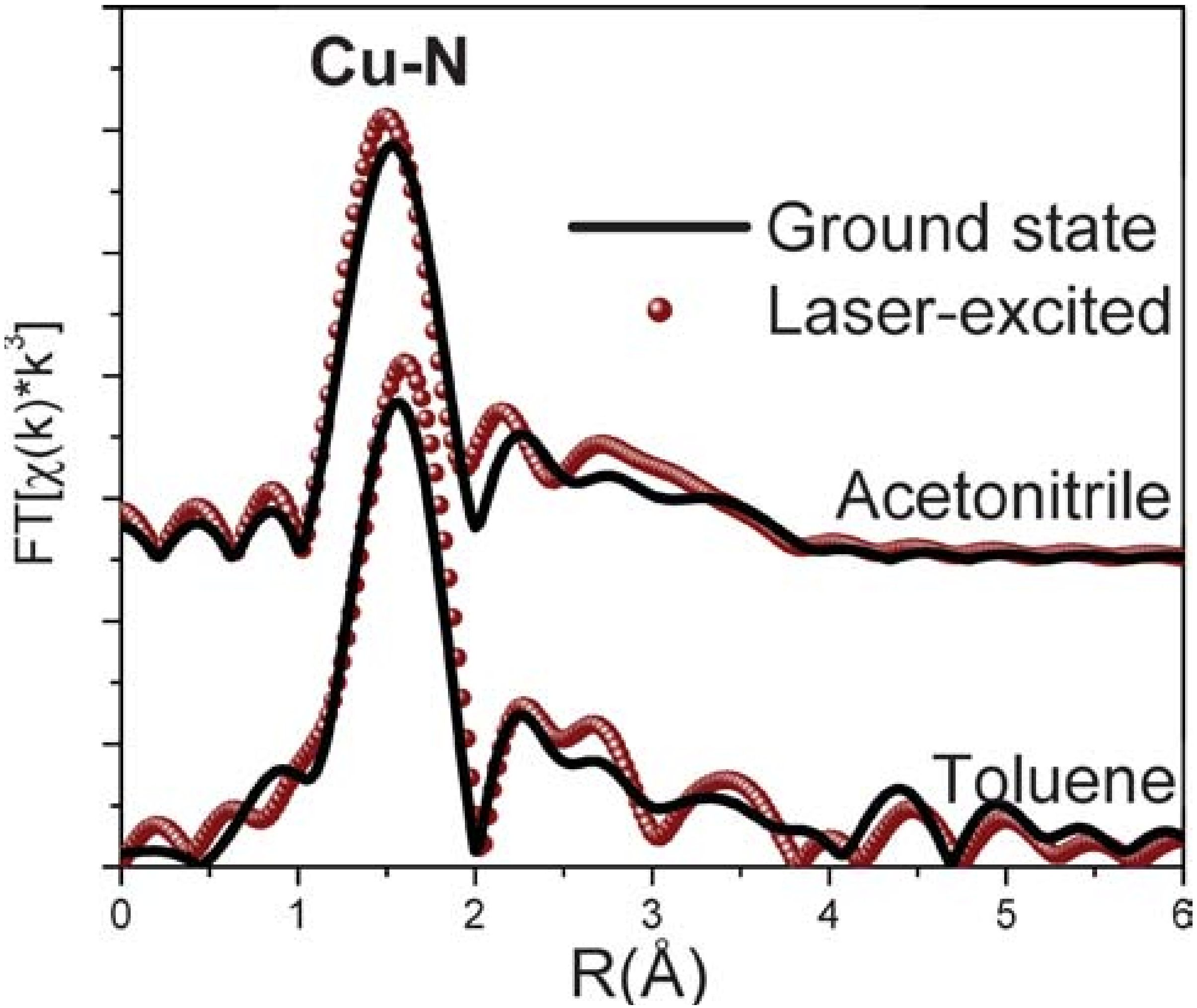
J. AM. CHEM. SOC. 2007, *129*, 2147−2160 ■ **2147**

XANES of $Cu(I)(dmp)_2$ in solution



L. X. Chen, Annual Reviews of Physical Chemistry, 56, 221-254 (2005).

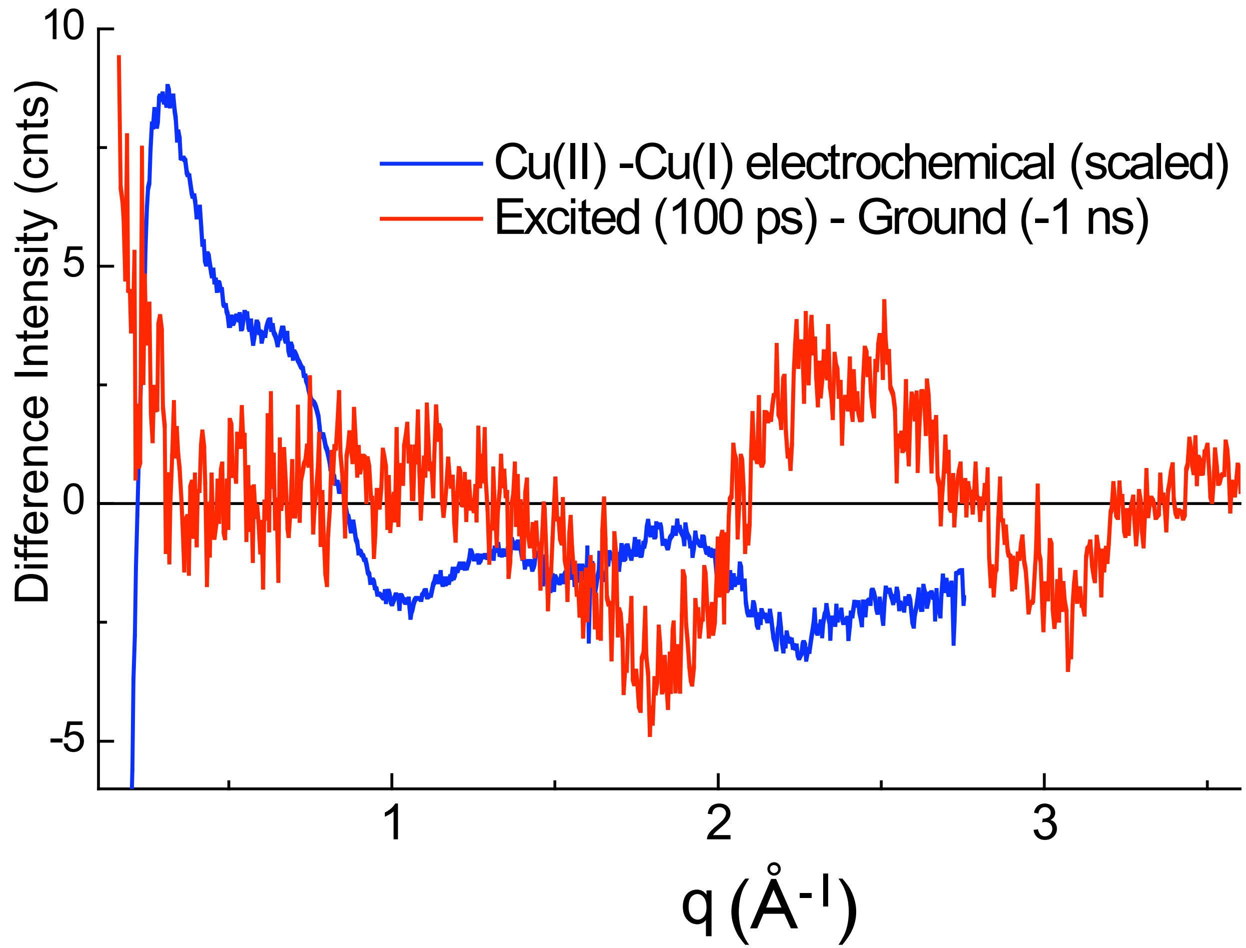
XAFS of Cu(I)(dmp)$_2$ in solution



L. X. Chen, Annual Reviews of Physical Chemistry, 56, 221-254 (2005).

Recent progress by L. Chen, Xiaoyi Zhang, D. Tiede, Klaus Attenkofer at APS-11-ID

Comparison electrochemical and Cu(I)DMP$_2$ excited state difference scattering patterns



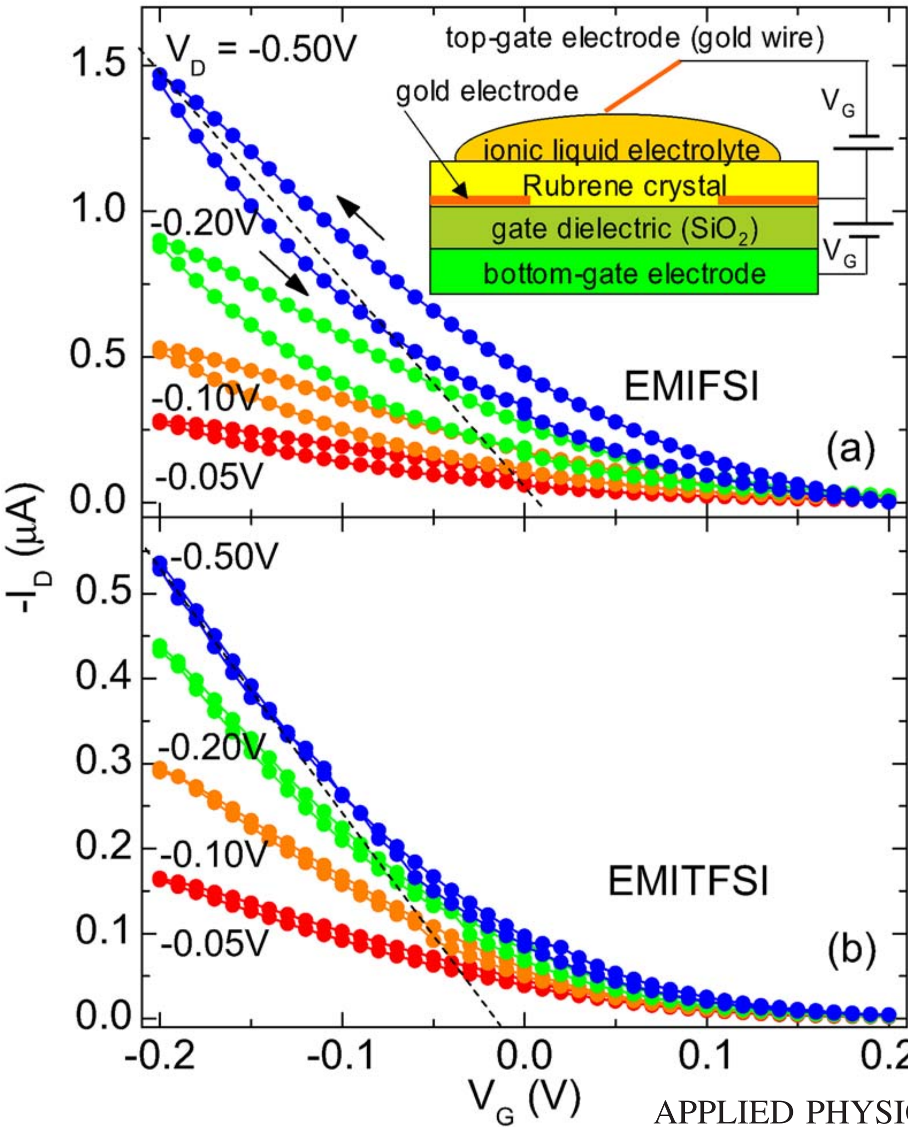
First Experiment (!):

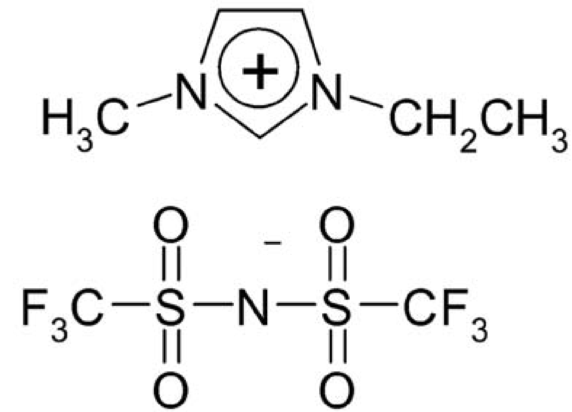
- **Clear excited state difference scattering**
- **Excited-state reorganization differs from ground state Cu(I)/C(II) reorganization**
- **Excited-state reorganization includes:**
  - Small angle: 5th ligand coordination (tris(hydroxymethyl)aminomethane)
  - High angle: heat + solvent reorganization

Applications of Laser-Induced Time-Resolved Small-Angle X-ray Scattering (LITR-SAXS):

Towards a Structural Understanding of Photo-induced Solvation and Charge-Transfer Processes in Ionic Liquids

Some Motivation for Understanding Structure and Dynamics in Ionic Liquids





High-density carrier doping
minimum gate voltages
high carrier mobility
fast-switching, low-power OFETs

APPLIED PHYSICS LETTERS **92**, 103313 (2008)

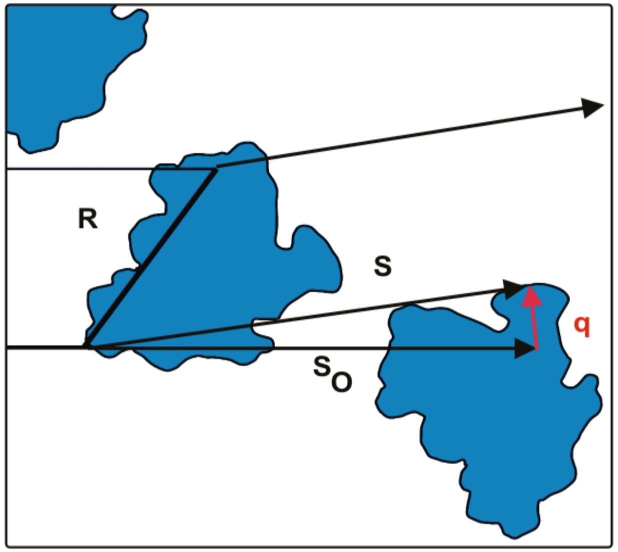
High-mobility, low-power, and fast-switching organic field-effect transistors with ionic liquids

S. Ono,[1,a)] S. Seki,[1] R. Hirahara,[2] Y. Tominari,[2] and J. Takeya[2,3]

SAXS / WAXS Structural Analysis

(slide from D. Tiede, ANL)

X-ray scattering in different angle regimes provides information about all levels of assembly structure



Small Angle X-ray Scattering (SAXS)

Size, shape, inter-particle correlations

$$\mathbf{I}(\mathbf{q}) = \int \mathbf{p}(\mathbf{r}) \frac{\sin(\mathbf{q}\,\mathbf{r})}{\mathbf{q}\,\mathbf{r}} \mathbf{dr}$$

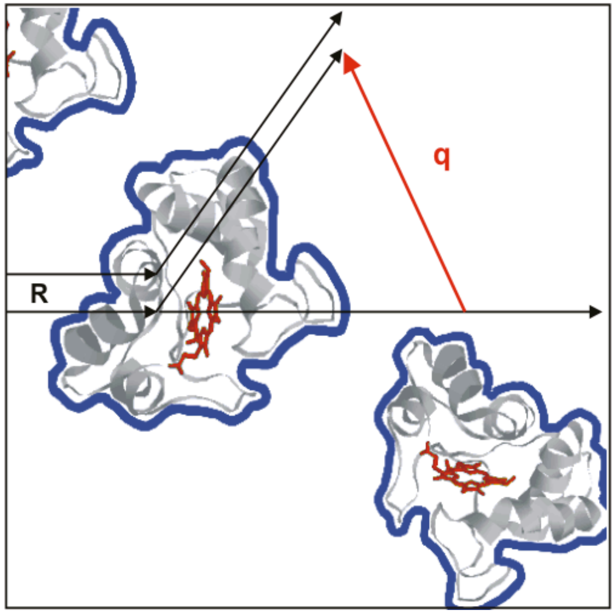
$$q = \frac{4\pi}{\lambda} \sin\theta$$

Guinier analysis to obtain electron-density weighted radius of gyration, R_g

$$\mathbf{I}(\mathbf{q}) = \mathbf{I}(\mathbf{0}) \exp\left(\frac{-\mathbf{q}^2 \mathbf{R_g}^2}{\mathbf{3}}\right)$$

Wide Angle X-ray Scattering (WAXS)

Internal atomic distance correlations



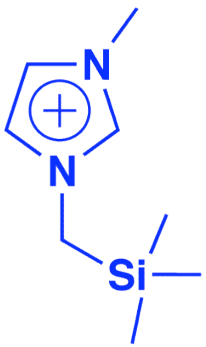
$$\mathbf{I}(\mathbf{q}) = \langle \mathbf{A}(\mathbf{q})^* \mathbf{A}(\mathbf{q}) \rangle \sum_{\mathbf{j}} \sum_{\mathbf{k}} \mathbf{f_j}(\mathbf{q}) \mathbf{f_k}(\mathbf{q}) \frac{\sin(\mathbf{q}\,\mathbf{r_{jk}})}{\mathbf{q}\,\mathbf{r_{jk}}}$$

$$\mathbf{f}(\mathbf{q}) = \iiint \mathbf{dV} \cdot \rho(\mathbf{r}) \exp(-\mathbf{iqr})$$

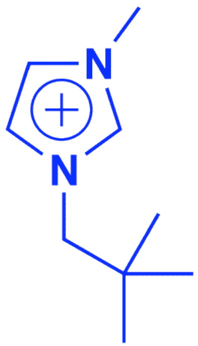
$$\mathbf{I}(\mathbf{q}) = \int \mathbf{p}(\mathbf{r}) \frac{\sin(\mathbf{q}\,\mathbf{r})}{\mathbf{q}\,\mathbf{r}} \mathbf{dr}$$

Pair distance distribution function (PDDF)

Examples of some novel Ionic Liquids

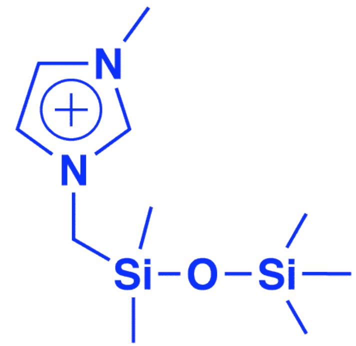


Si-mim$^+$



C-mim$^+$

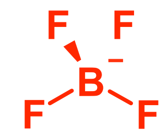
PhSi-mim$^+$

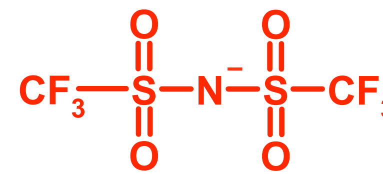


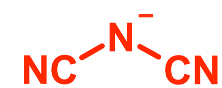
SiOSi-mim$^+$

cations

Br^- Cl^-



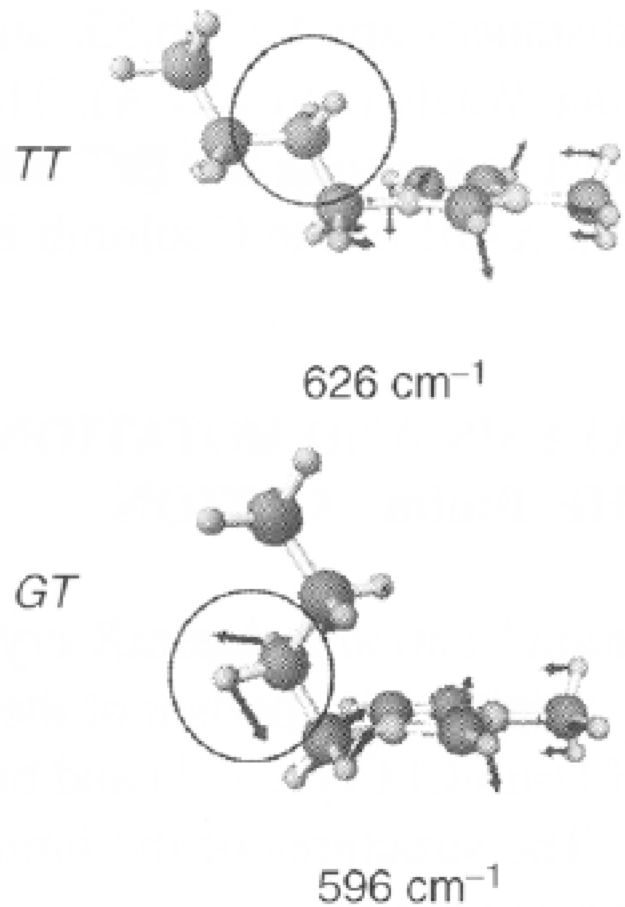


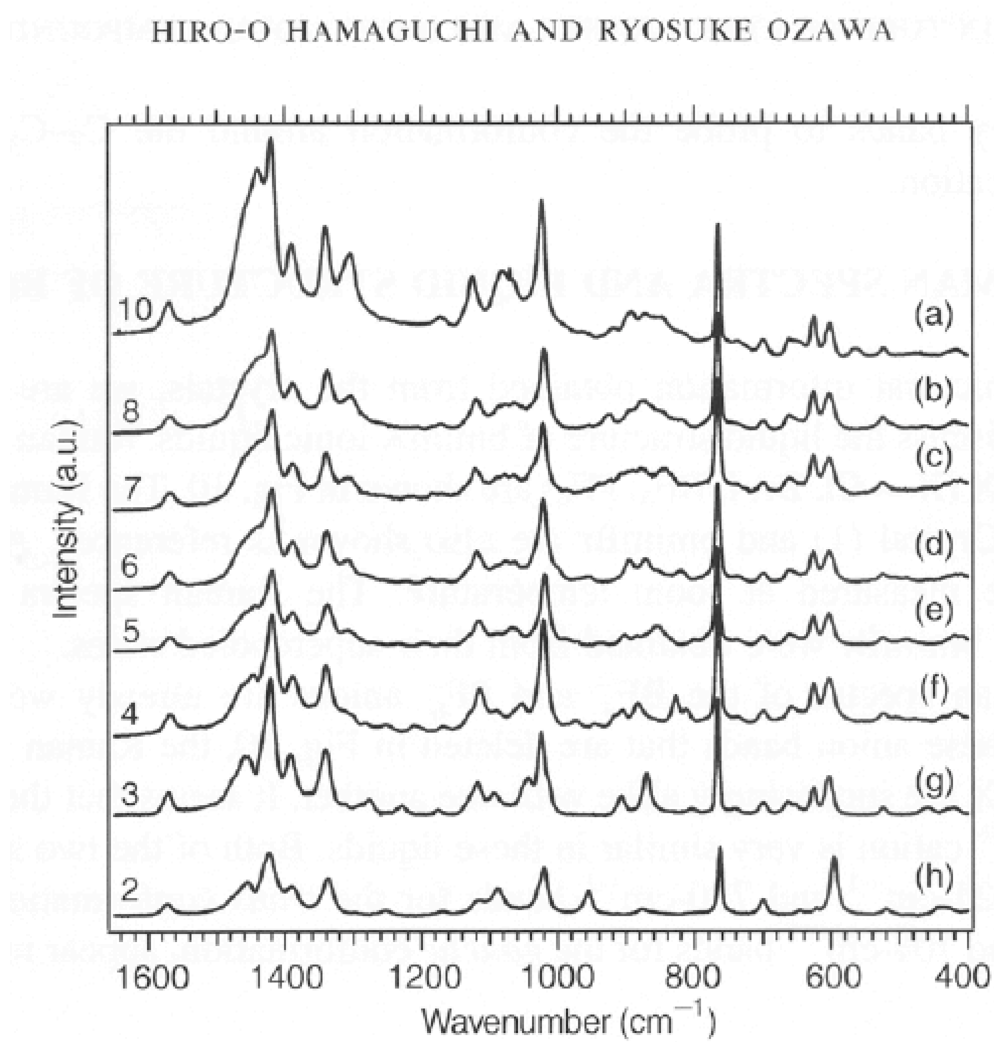


anions

H. Shirota and E. W. Castner Jr., *J. Phys. Chem. B* **2005,** *109*, 21576-21585
H. Shirota J. F. Wishart and E. W. Castner Jr., *J. Phys. Chem. B* **2007,** *111*, 4819-4829

Conformational Heterogeneity in Ionic Liquids



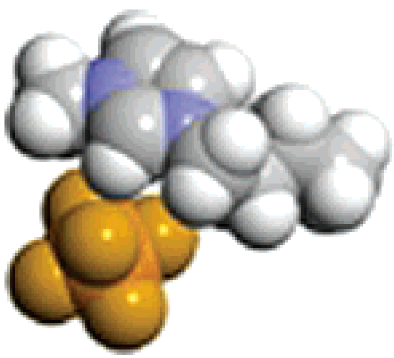


H. Hamaguchi and R. Ozawa, Adv. Chem. Phys., 131, 2005.

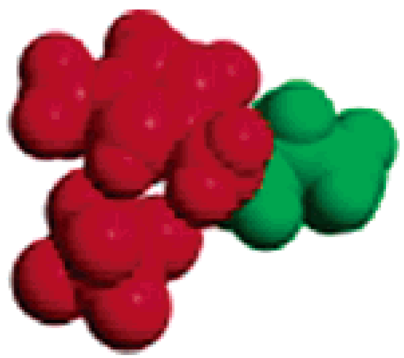
J. Phys. Chem. B **2006,** *110,* 3330−3335

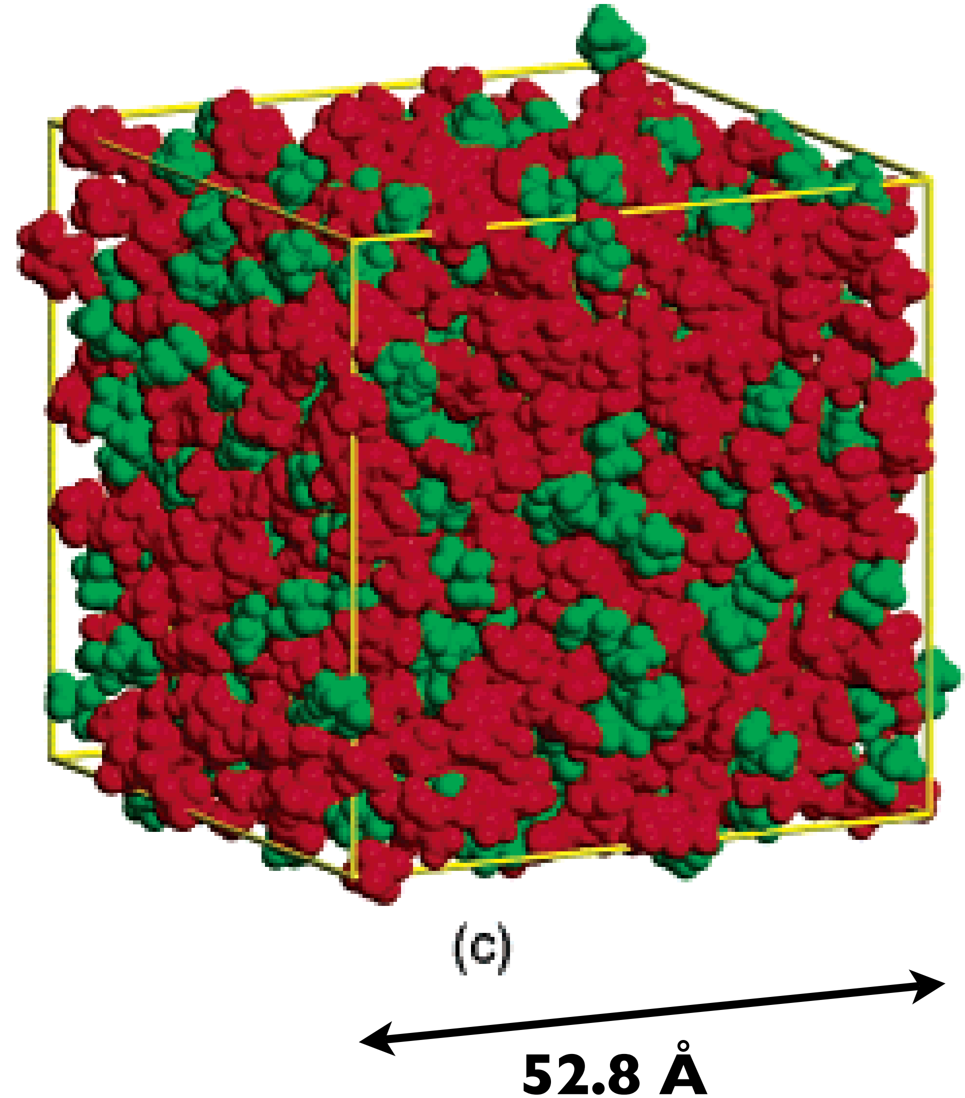
Nanostructural Organization in Ionic Liquids

José N. A. Canongia Lopes† and Agílio A. H. Pádua‡,*



C_4mim^+/PF_6^-



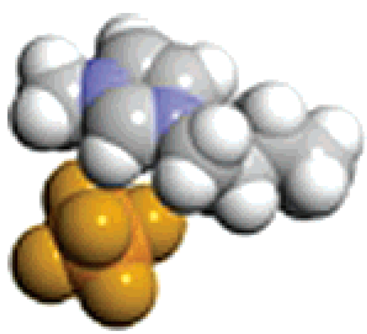


J. Phys. Chem. B **2007,** *111,* 4641−4644

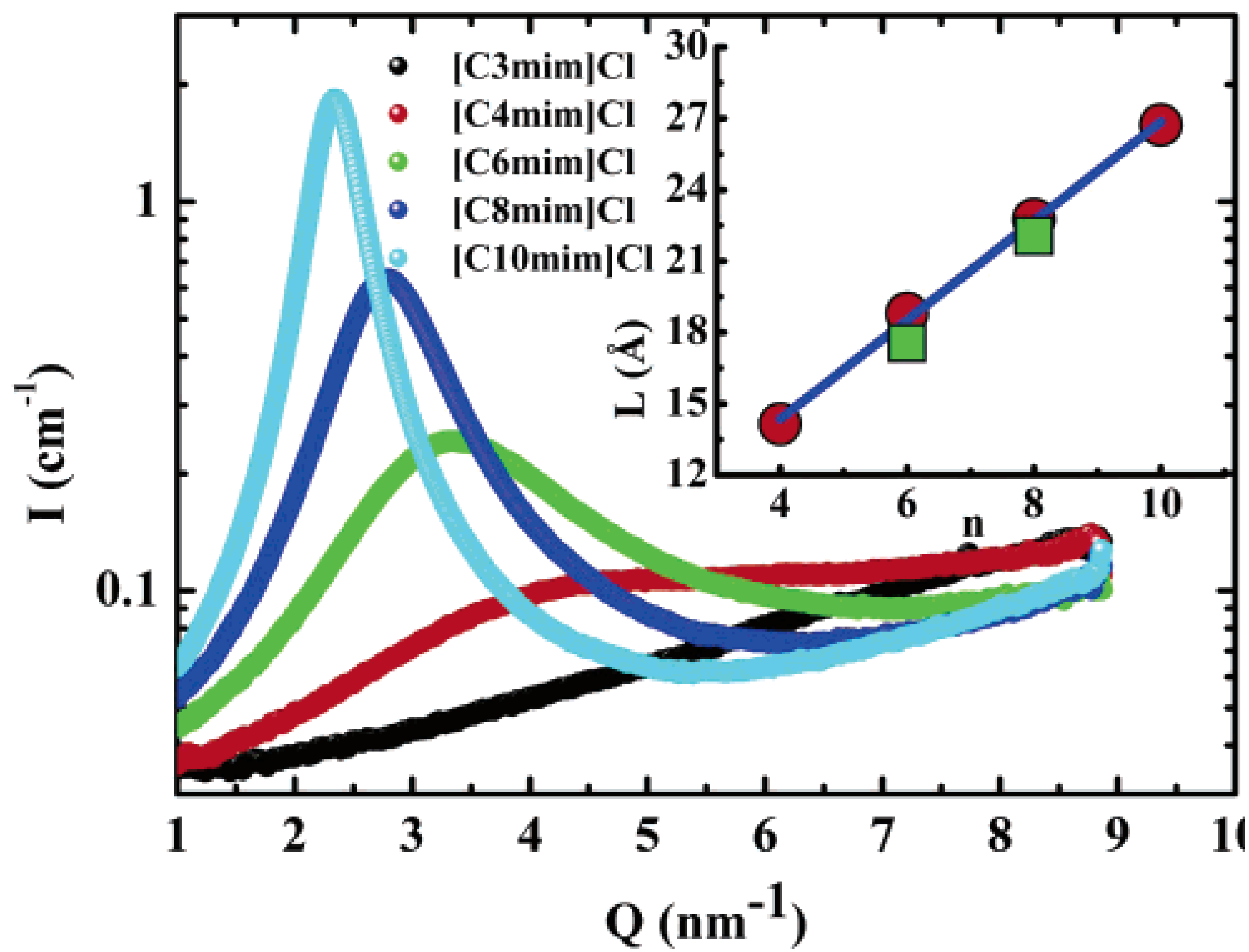
Nanoscale Segregation in Room Temperature Ionic Liquids†

Alessandro Triolo,*,‡ Olga Russina,§ Hans-Jurgen Bleif,§ and Emanuela Di Cola||

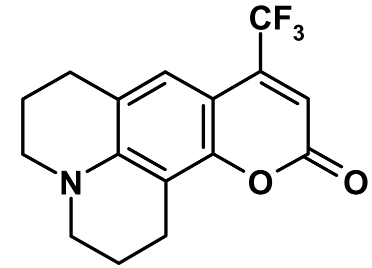
(Most-cited article in J. Phys. Chem. B for 2007)



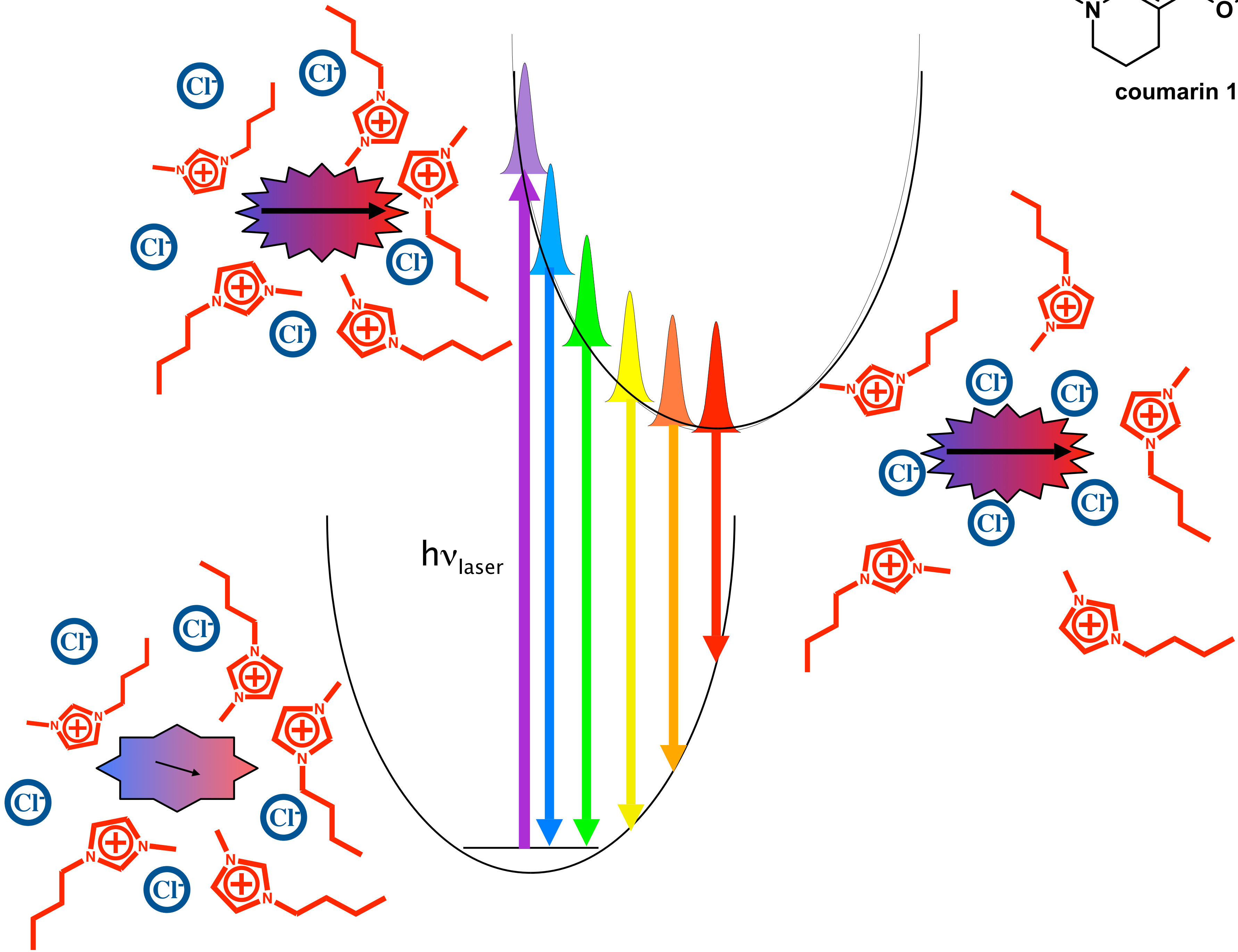
C_4mim^+/PF_6^-



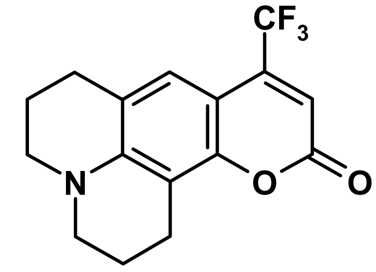
Translational solvation in ionic liquids



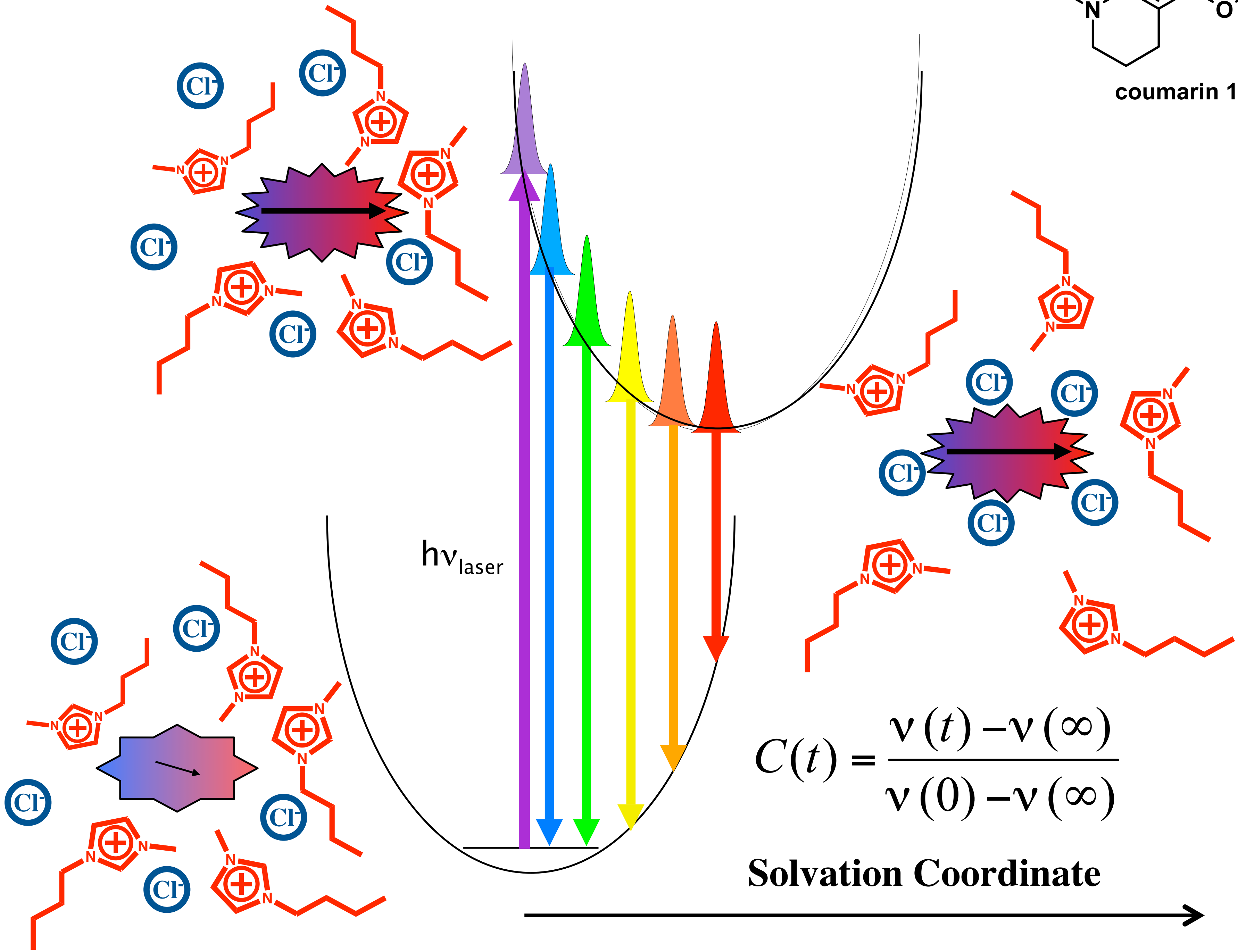
coumarin 153



Translational solvation in ionic liquids



coumarin 153



$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

Proposal:
LITR-SAXS studies of time-dependent translational dynamics in ionic liquids

Summary: Future Directions for Time-Resolved Structural Dynamics for Condensed-Phase Chemistry

**Laser-Induced Time-Resolved
X-ray Absorption Spectroscopy (LITR-XAS)**

**Laser-Induced Time-Resolved
Small-Angle X-ray Scattering (LITR-SAXS)**

**Laser-Induced Time-resolved X-ray Diffraction
(LITR-XRD)**